

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

No information is available in the TRI database on facilities that manufacture or process perchlorates because these chemicals are not required to be reported under Section 313 of the Emergency Planning and Community Right-to-Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986) (EPA 1997).

Commercial interest in perchlorates began in the late 1890s/early 1900s in Europe and the United States as a direct result of the pioneering efforts in rockets and their propulsion systems (Mendiratta et al. 1996). The production of ammonium perchlorate, the largest component of solid rocket propellants, far outpaced that of the other perchlorates listed in Table 4-1. Their commercial manufacture began later, and it was not until 1928 when GFS Chemicals began producing magnesium perchlorate for use as a desiccant (GFS 1997) that these salts became available on the U.S. market. Up until 1940, the total worldwide production of perchlorates had not exceeded 3.6 million pounds. An abrupt change in production was realized with the onset of World War II and the resulting increase in demand for rocket and missile propellants. Annual perchlorate production quickly increased to 36 million pounds because of this demand and remained at a high level thereafter (Mendiratta et al. 1996). By 1974, U.S. perchlorate production had reached 50 million pounds (Vogt 1986).

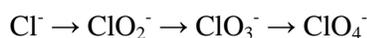
Recent production data for ammonium perchlorate as well as for the other salts listed in Table 4-1 are lacking. In 1994, U.S. production of ammonium perchlorate was estimated at 22 million pounds or just 36% of capacity (Mendiratta et al. 1996). These figures are on the same order of magnitude with those of the 1988 Department of Defense (DoD) and National Aeronautics and Space Administration (NASA) agreements with two U.S. suppliers to purchase 40 million pounds of ammonium perchlorate annually for the next 5–7 years (Anonymous 1988); these volumes were not ordered at the anticipated level due to reduced spending on space and defense programs (Kiesche 1994). Actual production volumes for ammonium perchlorate have been historically dependent on the demand of aerospace and military applications due to its predominant use in propellants (Mendiratta et al. 1996). This use has resulted in defining ammonium perchlorate as a strategic chemical (Mendiratta et al. 1996; Vogt 1986), and current worldwide production figures are not available nor would they be expected to be accurate.

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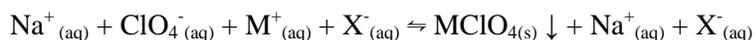
Accurate production volume data for magnesium, potassium, sodium, and lithium perchlorate could not be located. Approximately 900,000 pounds of ammonium perchlorate in aqueous solution serve as the feedstock for the production of magnesium and lithium salts for use in batteries (Mendiratta et al. 1996). The wide variety of uses for perchlorates (see Section 5.2) suggests that the combined production of the salts listed in Table 4-1 would be significantly higher. U.S. facilities listed in the SRI Directory of Chemical Producers that currently manufacture perchlorates are provided in Table 5-1. According to data listed on EPA's website, there were 63 Federal agency facilities and 168 non-Federal facilities in the United States that were either known or suspected perchlorate manufacturers/users as of April, 2003 (EPA 2005c).

No information is available in the Toxics Release Inventory (TRI) Database on facilities that manufacture or process perchlorates because these chemicals are not required to be reported under Section 313 of the Emergency Planning and Community Right-to-Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986) (TRI02 2005).

The predominant commercial method for the manufacture of perchlorates begins with the production of the most soluble salt, sodium perchlorate. Electrochemical oxidation of an aqueous solution of sodium chloride is the most common method of producing sodium perchlorate (Schilt 1979; Vogt 1986). Many variations for this process have been described over the years. They differ in the amount of current used, electrode composition, ionic strength of the bath, or temperature, although they all proceed via the following series of one-electron oxidations:



The manufacture of all other perchlorate salts, including those listed in Table 4-1, is accomplished by selectively re-crystallizing the perchlorate salts that are less soluble than sodium perchlorate. Thus, adding common salts to a solution of sodium perchlorate leads to a matathesis (ion exchange) process that is driven to the right as the desired product precipitates out of solution:



where M is magnesium, potassium, lithium, or ammonium; X is chloride, sulfate, or carbonate; and $\text{MClO}_{4(\text{s})}$ is the desired perchlorate. The majority of sodium perchlorate produced in the United States is converted to ammonium perchlorate using this process (Grotheer 1994).

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Table 5-1. U.S. Manufacturers of Perchlorates

Producer	Magnesium perchlorate	Potassium perchlorate	Ammonium perchlorate	Sodium perchlorate	Lithium perchlorate
GFS Chemicals, Inc. Columbus, Ohio 43222	√	√		√	√
Western Electrochemical Co. Cedar City, Utah 84720		√	√	√	
Barium and Chemicals, Inc. Steubenville, Ohio 43952		√			

Source: SRI 2004

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Given that the manufacture of perchlorates is typically accomplished in aqueous solution, the resulting perchlorate is produced as a hydrate. The anhydrous salt is required for pyrotechnic applications, and water molecules are removed from the hydrate by a number of methods including controlled heating, displacement of the water molecules by volatile amines (which are subsequently removed at reduced pressure or elevated temperatures), or through the use of a strong desiccant (Kamienski 1995). High purity perchlorate salts are produced by a wide variety of methods. For example, lithium perchlorate may be prepared by direct electrochemical oxidation of lithium chloride or by reaction of 70% perchloric acid with lithium carbonate (Kamienski 1995; Schilt 1979). A recent approach in the production of high purity ammonium perchlorate involves the electrolytic conversion of chloric acid to perchloric acid, which is then neutralized by ammonia gas (Mendiratta et al. 1996). The ammonium perchlorate is spray dried to the desired crystal size at air temperatures below 150 °C.

5.2 IMPORT/EXPORT

Data on the import and export of perchlorates could not be located in the available literature. The U.S. Census bureau does not list perchlorates as a separate, reportable item on its schedule B book on imports.

Perchlorates are known to be used in fireworks (see Section 5.3) and in 1997, U.S. imports of these pyrotechnic devices totaled \$93 million (U.S. Census Bureau 1999). U.S. exports of fireworks in 1997 totaled \$6.2 million. The actual volume of perchlorates represented by these figures is not known. Similarly, import/export volumes of perchlorates resulting from their use in the other products discussed in Section 5.3 are not available.

5.3 USE

The predominant uses of perchlorates take advantage of their strong oxidizing power and relative stability at moderate temperatures (Conkling 1996; Mendiratta et al. 1996; Schilt 1979; Vogt 1986). On heating, perchlorates decompose into chlorine, chlorides, and oxygen. As the reaction proceeds and temperatures increase, decomposition becomes self-propagating. In the presence of organics and other oxidizable materials (the fuel), large amounts of energy are released. The decomposition of ammonium perchlorate differs from that of the metal salts listed in Table 4-1 because it produces only the neutral products

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chlorine, water, oxygen, and nitrous oxide (or nitrogen oxide at high temperatures) and leaves no solid residue (e.g., sodium chloride residue is produced by the decomposition of sodium perchlorate).

Ammonium perchlorate is the largest volume perchlorate used in the United States (Mendiratta et al. 1996). Its primary use is as an oxidant for solid rocket boosters. The solid propellant used in the booster rockets on the U.S. Space Shuttle is approximately 70% ammonium perchlorate by weight (Conkling 1996). Accurate data on the total amount of ammonium perchlorate used in solid rocket boosters are not available, due in part to the strategic nature of its military and aerospace applications. Publically available information indicates that NASA and DoD contracted for 40 million pounds of ammonium perchlorate annually in the late 1980s/early 1990s (Anonymous 1988), although orders at this level were not realized (Kiesche 1994). It has been estimated that 90% of perchlorates that are produced are used for defense and aerospace activities (EPA website).

The other perchlorates listed in Table 4-1, most notably potassium perchlorate, also find use as oxidants in solid booster rockets (Lindner 1993). Oxidant mixtures developed using metal perchlorate salts are less powerful than those using ammonium perchlorate (Schilt 1979).

Perchlorates are used extensively in pyrotechnic devices. U.S. manufacturers shipped \$22.9 million worth of fireworks in 1992, up from \$15.3 million in 1987 (U.S. Census Bureau 1999), although the amount of perchlorate used in fireworks is not documented in the available literature. Ammonium perchlorate is used in small amounts in gun powder (Lindner 1993). Ammonium and potassium perchlorate are used in signal flares, including highway flares and marine signaling devices (Conkling 1996). Ammonium perchlorate is used in a mixture with sulfamic acid to produce a dense smoke or fog for military applications. Perchlorates are also used in civilian explosives.

It has been widely published in the scientific literature that perchlorates are used in airbag inflator systems (see, for example, Cowan 2000; Lamm et al. 1999; Logan 2001; Smith et al. 2001; Von Burg 1995). When used in this application, a chlorine scavenger would be required to prevent this gas from entering the passenger compartment (Maustellar 1996). Encyclopedic sources limit their discussion of airbag inflator systems to sodium azide (Antonsen 1996; Conkling 1996; Jansen 1992; Jobelios et al. 1989; Stiefel 1995), although potassium perchlorate has been used in compositions described as suitable for this purpose (Schilt 1979). Airbag inflators containing perchlorate have been described in the patent literature (see, for example, Scheffee et al. 1999); however, no source could be located in the available literature that specifically indicates commercial development of perchlorate containing systems. Given the well-

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known life-cycle of automobiles and the potential for perchlorate contamination that could result from its presence in this application, more information on its occurrence is required.

Perchlorates have also found use in a wide variety of other applications. They are used as oxygen generating systems (oxygen candles) for enclosed environments, such as submarines, spacecraft, and civilian and military aircraft (Vogt 1986). Anhydrous perchlorates, most notably the magnesium salt, is used as a highly efficient drying agent for gases as well as for scrubbing the last traces of polar compounds from inert gases (Schilt 1979). Lithium and magnesium perchlorate have been used in batteries due to their low weight and high energy density. Potassium perchlorate, mixed with a reactive metal such as iron or zirconium, has been used in heat pellets for the activation of reserve battery cells (Cohen 1993). Perchlorate salts are being investigated as additives for conducting polymers although they have been problematic due to their explosive nature (Druy 1986).

A novel use of ammonium perchlorate is as a component of temporary adhesives for steel or other metallic plates (Vogt 1986). Ammonium perchlorate is mixed with an epoxy resin, which, after curing, forms the adhesive bond between the plates. When separation of the plates is required, they are heated to initiate the self-propagating perchlorate decomposition, which, in turn, decomposes the epoxy adhesive (Vogt 1986).

Perchlorates find frequent use to adjust the ionic strength of electroplating baths (Schilt 1979). Metals that have been used in this process include aluminum and its alloys, iron, steel, nickel and its alloys, tin and lead alloys, and zirconium and its alloys. Perchlorate electrolysis baths are specifically used in plating razor blades. Perchlorates are also routinely used to adjust the ionic strength of aqueous solutions of analytical and investigative procedures of metal solutions (Nair et al. 1997; Papini and Majone 1997; Puls et al. 1992; Sposito and Traina 1987). They are used in this application because of the tendency of perchlorates not to form metal complexes in solution and, therefore, not to interfere with the chemical dynamics of the investigation (Cotton and Wilkinson 1980).

Perchlorates were widely used in the treatment of hyperthyroidism during the 1950s and early 1960s especially for people with Graves' disease (Von Burg 1995). Perchlorate is also available in the United States for administration (200–400 mg orally) to block radioactive technetium ($^{99}\text{TcO}_4^-$) uptake in the thyroid, choroid plexus, and salivary glands during medical imaging of the brain, blood, and placenta (Gibbs et al. 1998). Potassium perchlorate is currently used as part of a treatment to counter the thyroid effects of the drug amiodarone (Martino et al. 2001).

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Other uses for perchlorates include flares, matches, etching and engraving agents, photography, as a synthetic reagent (Sax and Lewis 1987), and in electrochemical machining (Vogt 1986). Lithium perchlorate has been described as a catalyst that should be used with caution for synthetic organic chemistry using the Diels-Alder reaction (Kamienski et al. 1995). Potassium perchlorate was used as an ignition ingredient in flash bulbs (Vogt 1986) and has been approved for use as an additive in rubber gaskets for food containers (FDA 1998). Perchlorates have also been used in weed killers and as growth promoters in leguminous plants. Ammonium, sodium, and potassium perchlorates have also been used as stimulants for increasing the weight of farm animals and poultry (Von Burg 1995).

Chilean saltpeter, a naturally occurring material proven to contain perchlorates (Schilt 1979), has been marketed mainly as a granular product for fertilizers (Laue et al. 1991). Chilean researchers initiated a study in 1967 to establish why soybeans were exhibiting stunted growth, rugose, and crumpled leaves as a result of domestic fertilizer application and to determine what levels of perchlorate these plants could tolerate (Tollenaar and Martin 1972). The saltpeter used to produce the fertilizer at that time contained 0.12–0.26% perchlorate (by weight) as a contaminant. The United States first began importing Chilean saltpeter in 1830 (Hoffmeister 1993). U.S. importers of the refined Chilean nitrate reached historic highs prior to 1980 (Bortle 1996), and current annual imports are at 2 million pounds (Laue et al. 1991). However, this amount represents <0.1% of the total amount of nitrogen fertilizer usage in the United States (Hoffmeister 1993). Fertilizer derived from Chilean saltpeter has been traditionally applied mainly to tobacco plants, but is also marketed for citrus fruits, cotton, and some vegetable crops (Urbansky et al. 2001). The amount of perchlorate present in recent samples of these fertilizers was found to range from 0.7 to 2.0 mg/g, although steps have been taken to reformulate these products to remove perchlorate.

In 1999, perchlorate was also detected in nine different brands of synthetic fertilizer products (Susarla et al. 1999a), raising concern for the potential widespread contamination from this source. The results of this study were questioned (Urbansky et al. 2000b) and a reinvestigation of many of the same products purchased at a later date found perchlorate in only one sample at a concentration 2 orders of magnitude lower than typically found in the original publication (Susarla et al. 2000). Nevertheless, it raised important questions as to why perchlorate would be present in synthetic fertilizers and how frequently it appeared. It also highlighted the difficulty in analyzing for perchlorate in solid samples and other complex matrices. Urbansky and Collete (2001) conducted a survey of approximately 40 fertilizer products comparing the results of six different laboratories. After an evaluation phase to determine the ability of each laboratory to quantify perchlorate in a fertilizer matrix, their results indicated that

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perchlorate was not detectable in any real-world fertilizer products (including synthetic fertilizers) that were not derived from Chilean caliche. During a survey of 48 fertilizer products collected from representative sites across the United States, perchlorate was detected in only 5 of the products (concentrations ranging from 1,800 to 4,200 µg/g) (EPA 2001).

5.4 DISPOSAL

In 1998, perchlorate was listed in the Drinking Water Contaminant Candidate List. The Safe Drinking Water Act, as amended in 1996, required EPA to publish a list of contaminants that were not subject to other primary drinking water regulation (EPA 1998a). In 1999, perchlorate was subsequently added to the Unregulated Contaminant Monitoring List that required public water systems that serve >10,000 persons, and other representative systems, to monitor for perchlorate and other substances beginning January, 2001 (EPA 1999b). The following year, EPA published a final rule indicating that standard method 314.0 should be used to monitor for perchlorate in drinking water (EPA 2000).

There are no other rules or regulations regarding the disposal of perchlorates.

Currently, there are no cost efficient removal processes to treat waste water containing perchlorates that can be applied on a wide scale. Conventional water treatment technologies, air stripping, activated carbon adsorption, chemical oxidation, and aerobic biodegradation are not efficient at removing perchlorate from water (Logan 1998; Urbansky 1998). Granular activated carbon columns do not economically remove the perchlorate anion from water. The useful lifetime of these columns was reduced from approximately 18 months to one month while treating tap water at the Texas Street Well facility in Redlands, California (Logan 2001).

The most promising physical removal process for treating perchlorate-contaminated water uses ion exchange technology (DoD 2005c, 2005d; EPA 2005e; Urbansky 2002). Perchlorate can be removed from water using ion exchange columns, although the resulting brine contains 7–12% perchlorate (Logan et al. 2001a). Currently, scientists are finding ways to improve this technology as well as to make it more cost efficient (Logan 2001). An ion exchange treatment facility has been installed at Edwards Air Force Base in California (DOE 2003). The DoD (2005c, 2005d) has reported that more than 9 million gallons of perchlorate contaminated groundwater have been successfully treated (perchlorate <4 ppb) since its implementation.

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Perchlorate removal using anaerobic bioreactors has been proven for onsite applications and at the pilot-plant level (Urbansky 1998), but has not yet established a proven track record in full-scale waste water treatment or for the treatment of contaminated groundwater. Research in this area is active (Bardiya and Bae 2005; Brown et al. 2003; Cramer et al. 2004; Logan and LaPoint 2002; Min et al. 2004). Suspended growth, fixed bed, and fluidized bed bioreactors have been used to degrade perchlorate at influent concentrations ranging from 0.13 to 7,750 ppb (Logan et al. 2001b). Abatement and remediation of perchlorate in soil and groundwater was achieved using a biological permeable reactive barrier system at the McGregor, Texas Naval Weapons Industrial Reserve Plant (Cowan 2000). According to the DoD (2005c, 2005d), a biological fluidized bed reactor installed at the Longhorn Army Ammunition Plant in Karnack, Texas is successfully reducing perchlorate levels in groundwater at the site to below the detection limit (<4 ppb).

Phytoremediation is another method being explored as a possible treatment process for perchlorate-contaminated soil, sediment, and water (Nzengung et al. 1999, 2004; Tan et al. 2004b; Urbansky 2002; Van Aken and Schnoor 2002). Plantings of lettuce and willow trees have been shown to reduce the concentration of perchlorate in contaminated soil (EPA 2004b; Nzengung et al. 1999, 2004; Yu et al. 2004).